Models of the Manganese Catalase Enzymes. Dinuclear Manganese(III) Complexes with the \([\text{Mn}_2(\mu-O)(\mu-O_2CR)_2]^{2+}\) Core and Terminal Monodentate Ligands: Preparation and Properties of \([\text{Mn}_2O(O_2CR)_2X_2(bpy)_2]\) (X = Cl\(^-\), N\(_3\)^- , H\(_2\)O)

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Abstract: Procedures are reported that allow access to dinuclear Mn\(^{III}\) complexes possessing the \([\text{Mn}_2(\mu-O)(\mu-O_2CR)_2]^{2+}\) core. The complexes have the general formulation \([\text{Mn}_2O(O_2CR)_2X_2(bpy)_2] (X = \text{Cl}^-, \text{N}_3^-, \text{H}_2\text{O})\) and are potential models of the Mn catalase enzymes. Treatment of MnCl\(_2/\text{bpy}/\text{acetic acid reaction mixtures in MeCN with NBu}_4\text{MnO}_2\) in MeCN leads to subsequent isolation of \([\text{Mn}_2O(O\text{Ac})_2\text{Cl}_2(bpy)_2] \cdot \text{AcOH} \cdot \text{H}_2\text{O}\) (1). Analogous reactions allow the preparation of \([\text{Mn}_2O(O\text{CF}_3)\text{Cl}_2(bpy)_2] \cdot 2\text{H}_2\text{O} (2)\) and \([\text{Mn}_2O(O\text{Et})_2\text{Cl}_2(bpy)_2] \cdot 3\text{EtCO}_2\text{H} \cdot \text{H}_2\text{O} (3)\). In the presence of \(\text{N}_3\), the complex \([\text{Mn}_2O(O\text{CF}_3)\text{Cl}_2(N_3)_2(bpy)_2] (4)\) is obtained; use of \text{AcO}^- and a greater \(\text{MnO}_2\) amount yields \([\text{Mn}_2O(N_3)_4(bpy)_2] (5)\) (6). Complex 1 can also be prepared from a reaction in which a solution of \(\text{Cl}_2\) in MeCN is employed as the oxidizing agent instead of NBu\(_4\text{MnO}_2\). If, however, aqueous HOAc is employed as the reaction medium, oxidation with an excess of \(\text{Cl}_2\) leads to \([\text{Mn}_2O(O\text{Ac})_2(\text{H}_2\text{O})_2(bpy)_2] \cdot \text{ClO}_4^- (6)\). The three \(\text{Mn}_2\) units are extremely similar and differ only in the identity of the terminal ligands \(X (\text{Cl}^-, \text{N}_3^-, \text{H}_2\text{O})\). They each contain a triply-bridged \([\text{Mn}_2(\mu-O)(\mu-O_2CR)_2]^{2+}\) core with chelating bpy and terminal X groups completing near-octahedral geometry at each Mn atom. In each case, the X group and an oxygen atom from a bridging \text{RCO}_2^- group lie on a Jahn–Teller elongation axis (high-spin \(\text{Mn}^{III}\)). Complexes 1, 2, 3, and 5 have been studied by cyclic voltammetry in DME; each display a quasi-reversible oxidation at \(-0.4\) V (1, 2, and 3) and \(0.18\) V (5) vs ferrocene, assigned to the \(2\text{Mn}^{III}/2\text{Mn}^{II}\) couple. Variable-temperature solid-state magnetic susceptibilities of 1 and 5 were measured in the temperature range 5.0 to 330 K. The effective magnetic moment per Mn\(^{III}\) (\(u_M\)) for 1 decreases gradually from 6.33 \(\mu_B\) at 327.7 K to 5.85 \(\mu_B\) at 100 K and then more steeply to 2.09 \(\mu_B\) at 5.0 K. For 5, \(u_M\) increases steadily from 6.96 \(\mu_B\) at 320 K to a maximum of 8.12 \(\mu_B\) at 30 K and then decreases to 7.45 \(\mu_B\) at 5.0 K. The data were fit to a model that included an isotropic Heisenberg exchange interaction, an isotropic Zeeman interaction, and axial zero-field splitting terms for both ions. For complex 1, a fit was found with \(J = -4.1\) cm\(^{-1}\), \(g = 1.88\), \(D_1 = D_2 = -0.07\) cm\(^{-1}\), and 0.8% by weight of a paramagnetic \(S = 2\) impurity. For complex 5, the corresponding values are \(J = +8.8\) cm\(^{-1}\), \(g = 1.86\), and \(D_1 = D_2 = 0.3\) cm\(^{-1}\); the quality of the fit is less than that for 1, and this was concluded to be due to the presence of \(\text{intermolecular exchange interactions propagated by the intermolecular hydrogen-bonding network observed in the crystal structure of 5-MeCN+H}_2\text{O}\). Thus, 5 is ferromagnetically coupled and has an \(S = 4\) ground state. The \(J\) values for all available complexes containing the \([\text{Mn}_2O(O_2CR)_2]^{2+}\) core are compared, and a rationalization is suggested for the differences between 1/7 (negative \(J\)) and 5 (positive \(J\)). The relevance of these results to Mn catalase are discussed as well as to the observed difference in sign of the \(J\) values for deoxyhemerythrin (negative \(J\) versus deoxy-N\(_3^-\)hemerythrin (positive \(J\)).

Introduction

It is now well established that a number of Mn-containing metalloenzymes contain tightly-bound Mn ions that are involved in the enzyme function.\(^3\) These include certain bacterial superoxide dismutases, catalases, and ribonucleotide reductases and the photosynthetic water oxidation center of green plants and cyanobacteria.\(^2\) Of particular relevance to this work are the catalases\(^2,3\) and ribonucleotide reductase\(^4,5\) whose study is still in its infancy, but which appear to possess a dinuclear Mn\(_2\) site, as confirmed by preliminary X-ray crystallographic studies on the \(\text{Thermus thermophilus}\) enzyme.\(^6\) These complement detailed studies by other techniques that are strongly indicative of dinuclear sites.\(^3,5\) On the basis of spectroscopic evidence, the manganese is thought to occur in a \([\text{Mn}_2(\mu-O)(\mu-O_2CR)_2]^{2+}\) core with N-based (histidine imidazole) peripheral ligands; evidence for the latter is beginning to appear.\(^6\) As a result, a number of groups initially reported the preparation and characterization of Mn\(^{III}\)


complexes with the [Mn2O(O2CR)2]2+ core and two tridentate N-based ligands capping each end of the molecule. Modeling studies employing tridentate ligands have been important in establishing the accessibility of the [Mn2O(O2CR)2]2+ unit within synthetic complexes, but by blocking all three terminal coordination sites at each manganese, they preclude investigation of substrate or substrate–analogue binding studies. It was the goal of this study to prepare similarly bridged dinuclear complexes employing the bidentate ligand 2,2'-bipyridine (bpy), thus leaving a coordination site available for binding additional ligands; this strategy has already proven successful in FeIII chemistry where bpy has allowed access to hemerythrin model complexes [Fe2O(0Ac)2Cl2(bpy)] and [Fe2O(C6H4Ph)(N3)2(bpy)] and, subsequently, [Fe2O(mdp)Cl2(4,4'-Me2bpy)] (mpdH2 = m-phenylenediaminopropionic acid). A preliminary communication has reported our subsequent success in preparing \([\text{MnZO(OAc)}_{2}(\text{H}_{2}\text{O})_{2}(\text{bpy})_{2}]^{2+}\) and [Mn2O(O2CPh)2(bpy)2]2+.

We herein describe a variety of synthetic procedures that have allowed access to these complexes, including a high yield procedure to Girerd's bis-aquo cation, together with their structural characterization. This trio of complexes represents a great opportunity to investigate systematically the influence of the Cl-/N2/H2O groups on the structural and magnetic properties of the \([\text{Mn2O(O2CR)}_{2}]^{2+}\) core.

**Experimental Section**

**Compound Preparation.** All chemicals and solvents were used as received; all preparations were performed under aerobic conditions. NBu4-MnO4 was prepared as described elsewhere.13 Solutions of Cl2 in MeCN were prepared by bubbling a calculated mass of Cl2 into MeCN in a 100-mL volumetric flask and making up to the mark with MeCN. The resulting solution was standardized iodometrically and stored in a stoppered flask at room temperature. The crystals were not dried and spectral comparison with material obtained as described below.

**Method A.** To a stirred solution of MnCl2•4H2O (1.61 g, 8.14 mmol) and bpy (2.00 g, 12.8 mmol) in MeCN (30 mL) and acetic acid (6 mL) was added solid NbBu4MnO4 (1.95 g, 5.40 mmol) in small portions. The resulting homogeneous, dark brown solution was slowly concentrated by evaporation to dry. The identity of the product was confirmed by crystallography and by electronic and spectral comparison with material obtained as described below.

**Method B.** To a slurry of complex I (0.35 g, 0.50 mmol) in MeCN (30 mL) was added solid benzoic acid (0.25 g, 2.0 mmol). The resulting brown solution soon began to precipitate dark red microcrystals, and, after 2 h, they were collected by filtration, washed with Et2O, and dried in air: yield ~59%; electronic spectrum in DMF 280 (1.7 × 103), 340 (sh, 740), 502 (sh, 135); IR data (Nujol) 3400 (br, 2300), 1730 (s), 1600 (s), 1510 (m), 1450 (m), 1370 (m), 1260 (m), 1230 (m), 1170 (m), 1100 (m), 1070 (m), 1030 (m), 930 (s), 830 (s), 721 (s), 585 (s), 565 (s). Anal. Caled for C35H30N4O7Cl2Mn2: C, 51.86; H, 3.84; N, 17.09.

**Method C.** To a slurry of Mn(Br)2•4H2O (4.23 g, 8.12 mmol) and bpy (2.00 g, 12.8 mmol) in MeCN (30 mL) and propionic acid (6 mL) was added solid NbBu4MnO4 (1.95 g, 5.40 mmol) in small portions. The resulting homogeneous, dark brown solution was filtered and left undisturbed at ambient temperature for several hours. The black crystals were collected by filtration, washed with Et2O, and dried in air: yield ~50%; electronic spectrum in DMF 283 (7 × 103), 468 (sh, 275), 721 (s), 725 (s), 1730 (s), 1600 (s), 1510 (s), 1450 (m), 1370 (m), 1250 (m), 1170 (m), 1100 (m), 1070 (m), 1030 (m), 930 (s), 830 (s), 721 (s), 585 (s), 565 (s). Anal. Caled for C35H30N4O7Cl2Mn2: C, 51.86; H, 3.84; N, 7.12; Cl, 9.0. Found: C, 50.9; H, 3.9; N, 7.1; Cl, 9.3.

**Conclusion**

The sample for crystallography was obtained from a separate preparation. The crystals were not dried in vacuo, and the crystallographic study established the formulation \(5\text{MeCN}.4\text{H}_{2}\text{O}.\)

In subsequent stages, each molecule of the asymmetric unit and H2O were located in the asymmetric unit. A difference Fourier at this stage revealed some hydrogen atoms, but no attempt to refine them was made; instead, hydrogen atoms were included as fixed-atom contributors, except for those of the solvent molecules which were omitted. The final difference map was essentially featureless. Final values of conventional indices R and Rw are included in Table I.

For complexes 5-MeCN-H2O and 7, a systematic search of limited hemispheres of reciprocal space located sets of diffraction maxima that exhibited monomeric symmetry. The systematic absences of hkl for \( h+2k + 2n = 1 \) identified the space group as either \( P2_1 \) or \( Cc \). The choice of the centrosymmetric space group \( P2_1 \) was confirmed by the successful solution and refinement of the structures.

For complex 5, the dinuclear unit lies on a crystallographic 2-fold axis passing through bridging oxygen atom O(23); the asymmetric unit thus consists of the whole molecule, together with two molecules of H2O and half a molecule of CH2CN, the methyl carbon of which lies on the 2-fold axis. All non-hydrogen atoms were readily located and refined with anisotropic thermal parameters except for the MeCN molecule which was refined isotropically. All hydrogen atoms were included in the latter stages as fixed-atom contributors except for those of the solvents, which were omitted. The final difference map was essentially featureless. Final values of R and Rw are included in Table I.

In contrast, complex 7, the asymmetric unit contains the dinuclear unit and two monomers. All non-hydrogen atoms were readily located and refined anisotropically with no disorder problems being encountered; all hydrogen atoms were visible in a subsequent difference Fourier phased on the non-hydrogen atoms. The hydrogen atoms were included in the final cycles and refined isotropically. The hydrogen atoms of the water molecules were somewhat ill-behaved, exhibiting large thermal parameters, but their removal increased the discrepancy indices slightly, and the hydrogen atoms reappeared in subsequent difference Fourier maps, so they were reincorporated. The final difference map was essentially featureless. Final values of R and Rw are included in Table I.

### Physical Measurements

Variable-temperature DC magnetic susceptibility data were measured by using a Quantum Design MPMS SQUID magnetometer equipped with a 3.5 T magnet. The susceptometer was operated at a magnetic field strength of 10 kG. Diamagnetic corrections were estimated from Pascal’s constants and subtracted from the experimental susceptibility data to obtain the molar paramagnetic susceptibilities of the compounds. These susceptibilities were fit to the appropriate theoretical expressions by means of a least-squares-fitting computer program.

### Results

### Syntheses

Previous work had established NBu₄MnO₄ as a useful new reagent for the synthesis of nonaqueous media of Mn complexes in the oxidation state range II–IV and with various nuclearities. The synthetic strategy is a coordination reaction between MnO₄⁻ and MnII in the presence of appropriate...
ligands and in MeCN, EtOH, or DMF (or combinations thereof) as reaction solvent. Of particular relevance to the present work was the observation\(^{(1)}\) that NBu\(_4\)MnO\(_4\), Mn(OAc)\(_2\), NBu\(_4\)ClO\(_4\), PhCOOH, and bpy in MeCN lead directly to high yields (\(\sim 60\%\)) of the tetroxane complex [Mn\(_2\)(O\(_2\)CPH\(_2\))(bpy)\(_2\)](ClO\(_4\)) originally prepared\(^{(15)}\) by the reaction of bpy with preisolated [Mn\(_2\)O\(_2\)(O\(_2\)CPH\(_2\))(py)]\(_2\)(ClO\(_4\)). In a subsequent experiment, it was discovered that the at-first-glance trivial replacement of Mn-(OAc)\(_2\) with MnCl\(_2\) led to a completely different product. No sign of the red color of the tetroxane complex was observed; instead, concentration of the brown reaction solution led to isolation of black crystals identified as complex 2. Addition of a cosolvent was avoided as this causes precipitation of reaction byproducts, leading to messy mixtures difficult to purify. A more convenient procedure to 2 is ligand exchange with I\(_{-}\) (95% yield), as described below (vide infra). Subsequent extension of this method to acetic and propionic acids allowed access to the corresponding complexes 1 and 3, respectively. Complex 1 was structurally characterized confirming the formulation [Mn\(_2\)-(OAc)\(_2\)]Cl\(_2\)(bpy)\(_2\)·AcOH·H\(_2\)O.

The [Mn\(_2\)(μ-O)(μ-Cl)]\(_3\) unit in complexes 1-3 represents one-half of the [Mn(μ-O)(μ-Cl)]\(_4\) core in the tetracation [Mn\(_2\)(O\(_2\)ClO\(_4\))\(_2\)(bpy)\(_2\)]\(_2\)\(^{2+}\). The presence of the Cl\(^{-}\) ions provided by MnCl\(_2\) can thus be considered as "trapping" the dinuclear fragment preventing dimerization to Mn\(_4\)O\(_8\)-containing products. We make no firm mechanistic implication by this statement, however, since there is no direct evidence that Mn\(_2\)O species are intermediate in the formation of the tetranuclear materials (vide infra). Note that complex 1 is also the product when Mn(OAc)\(_2\) is used in the reaction in the presence of NET\(_4\)-Cl, so that 1 is not formed because of the absence of free AcO- ions in the medium.

Extension of the above procedure to other halides has been explored. When the reaction was carried out using NBu\(_4\)F instead of NET\(_4\)-Cl, the presence of F\(^{-}\) appeared (visually) to also suppress formation of red [Mn\(_2\)(OAc)\(_2\])(bpy)\(_2\)]\(^{2+}\), but it proved difficult to isolate and identify the product(s); black oils were repeatedly obtained that proved difficult to purify. With MnBr\(_2\), a black crystalline precipitate was obtained that proved to be complex 4 in 60% isolated yield; i.e., the [Mn\(_2\)(OAc)\(_2\)](bpy)\(_2\)\(^{2+}\) moiety was now formed. The use of I\(_{-}\) was also unsuccessful; it is too good a reducing agent for higher oxidation state Mn and did not yield any higher oxidation state (II) product. Overall, the use of Cl\(^{-}\) appears to be the optimum method for diverting the reaction to the dinuclear products and allowing their isolation in pure form.

The complex [Mn\(_2\)(OAc)\(_2\)]([Br(pz)\(_2\)])\(_3\), containing a similar [Mn(μ-O)(μ-OAc)]\(^{2+}\) core as 1, has been shown to undergo facile carboxylate exchange.\(^{(7)}\) Complex 1 displays similar reactivity, as shown by its reaction with excess PhCOOH which converts it, essentially quantitatively (95% isolated yield), to 2, as summarized in eq 1. No complicating side reactions involving the Mn-Cl bonds are thus occurring, as

\[
[Mn\text{O}(OAc)\text{Cl}_2(bpy)_2] + 2PhCOOH \rightarrow [Mn\text{O}(O_2\text{CPH}_2)\text{Cl}_2(bpy)_2] + 2\text{HOAc (1)}
\]

had seemed a possibility. Similar carboxylate-exchange reactions have also been seen for [Mn\(_2\)(OAc)(bpy)]\(^{4+}\) and [Mn\(_2\)-O-(OAc)-(pic)]\(^{-}\)\(^{15,19}\).

At this point, we wondered whether similar dinuclear species could be isolated with "pseudohalide" monoanionic ligands. Azide was the ligand of choice because of its biological relevance, being an inhibitor of certain catalases.\(^{(4)}\) The presence of N\(_3\)\(^{-}\) in a related reaction mixture led to isolation of complex 5, the formulation of which as [Mn\(_2\)(O\(_2\)CPH\(_2\))(N\(_3\)\(_2\))(bpy)\(_2\)] was confirmed by crystallography. Interestingly, however, attempts to make the corresponding AcO- complex instead yielded complex 6, Mn\(_2\)-O-(N\(_3\)\(_2\))(bpy)\(_2\). Structural characterization of 6 was thwarted by the instability of larger crystals (explosively, on one occasion) although microcrystalline material is well behaved. In accord with the analytical composition, it seems reasonable that this is a Mn\(_{IV}\) dimer with two μ-O\(^2\) groups and a bpy and two N\(_3\)\(^{-}\) ligands terminally coordinated to each Mn. There are now several examples of the [Mn\(_2\)(μ-O\(_2\))]\(^{4+}\) core bound to exclusively N-based peripheral ligands.\(^{(4)}\)

An additional reactivity characteristic established to date for complex 1 involves its behavior in aqueous solution. Dissolution of 1 in a minimum of water followed by immediate removal of solvent under vacuum yields a brown powder. This product was concluded to be the Mn\(_{III}\) complex 8, [Mn\(_2\)(OAc)\(_2\)](bpy)\(_2\)]\(^{4+}\), based on analytical data and spectroscopic comparison with authentic material.\(^{(14)}\) The effect of brief dissolution in water is thus the hydrolytically-induced formation of a higher oxidation state product, probably via disproportionation. Similar behavior under similar conditions has previously been reported\(^{(20)}\) for [Mn\(_2\)-O-(OAc)\(_2\)](TACN)\(^{4+}\) (TACN = 1,4,7-triazacyclononane), which hydrolyzes in water to yield [Mn\(_2\)(OAc)(TACN)]\(^{4+}\). The ~60% yield of 8 is consistent with eq 2, the Mn\(_{II}\) byproduct being removed in the

\[
3\text{Mn}_{II} + \text{H}_2\text{O} \rightarrow 2\text{Mn}_{III} + 2\text{Mn}_{II} (2)
\]

wash. Again, the presence of Mn-Cl linkages in 1 does not provide complicating side reactions; all chemistry seems to be concentrated in the bridging region.

It was proposed above that the Cl\(^{-}\) ion functions to "trap" the dinuclear [Mn\(_2\)] fragment, preventing its aggregation to a [Mn\(_4\)] product. If so, it seemed reasonable to suspect that, under appropriate conditions, preisolated 1 could be converted to a tetranuclear species. This has now been demonstrated. Treatment of 1 with acetic acid and NaOAc, the latter to help sequester Cl\(^{-}\) as NaCl, led to the characteristic red coloration of [Mn\(_4\)]\(^{4+}\) complexes; addition of ClO\(_4\)\(^{-}\) led to isolation of known\(^{(15)}\) [Mn\(_2\)(OAc)\(_2\)](bpy)\(_2\)](ClO\(_4\))·3H\(_2\)O in 56% yield. The conversion can be summarized in eq 3; the HOAc was essential for high yield conversion.

\[
2[Mn\text{O}(\text{OAc})\text{Cl}_2(bpy)_2] + 4\text{NaOAc} \rightarrow [\text{Mn}\text{O}_2(\text{OAc})_4(bpy)_2]^{2+} + 2\text{bpy} + \text{AcO}^- + 4\text{NaCl (3)}
\]

This transformation lends some support for the possibility that, in the absence of Cl\(^{-}\), the synthetic procedure that leads directly to [Mn\(_4\)]\(^{4+}\) products from Mn\(_{II}\) and Mn\(_{III}\) reagents does proceed via the intermediacy of [Mn\(_2\)]\(^{4+}\) units. Attempts to effect the reverse reaction, i.e., cleavage of [Mn\(_2\)(OAc)\(_2\)](bpy)\(_2\)]\(^{4+}\) with Cl\(^{-}\) and bpy to yield complex 1, have proven unsuccessful.\(^{(21)}\)

**Syntheses Using Elemental Chlorine.** It has been discovered that the NBu\(_4\)MnO\(_4\) may be replaced with other oxidizing agents. Elemental Cl\(_2\), dissolved in MeCN, has provided a preparative route (method C) to higher yields of complex 1 (~40%) than that available from the comproportionation procedures. Thus, addition of 0.5 equiv of Cl\(_2\) to Mn(OAc)\(_2\)-4H\(_2\)O and bpy in MeCN/HOAc yields the Mn\(_{III}\) complex 1, as expected from eq 4. Addition of only 0.25 equiv of Cl\(_2\) leads to lower yields of 1

\[
2\text{Mn}_{II} + \text{Cl}_2 \rightarrow 2\text{Mn}_{III} + 2\text{Cl}^- (4)
\]

rather than a Mn\(_{II}\), Mn\(_{III}\) product. If either 0.75 or 1.0 equiv of Cl\(_2\) are used, the brown solution undergoes a further color change to dark green, characteristic of a Mn\(_{IV}\)-containing product, and an olive-green, sparingly-soluble powder is precipitated. The latter


\[\text{(21)}\] In contrast to the behavior of the analogous Fe\(_2\) complex, which is converted to an Fe\(_3\) product, see ref 9.
appears similar but not identical to complex 8. The low solubility of this product has hitherto foiled attempts at purification and/or crystallization.

In contrast to the results in MeCN/HOAc, parallel reactions in H₂O/HOAc have led to only Mn₃⁺ products, even in the presence of an excess of Cl₂. Thus, bubbling of Cl₂ through an aqueous HOAc solution of Mn(OAc)₂·4H₂O and bpy gives a dark brown solution from which may be isolated complex 7 in high yield (74%) on addition of NaClO₄. The cation has already been reported as the PF₆⁻ salt by Girerd and co-workers from a comproportionation reaction in aqueous MeOH. The present procedure is particularly facile and high yield. Because of the low solubility of Cl₂ in H₂O, quantitative addition of aqueous Cl₂ solutions was not attempted; however, prolonged bubbling of Cl₂ through the reaction mixture gave the same product, 7.

Other water-soluble oxidizing agents were also briefly explored. Addition of 1/4 equiv of NaIO₄ to the aqueous HOAc solution of Mn(OAc)₂·4H₂O/bpy rapidly led to a dark brown solution and isolation of 7 on addition of NaClO₄. Greater amounts of NaIO₄ led to mixtures of 7 and an unidentified red-brown solid. Similarly, addition of 1 equiv of (NH₄)₂S₂O₇ not only led to slower formation of a dark brown solution but also then gave 7 on addition of NaClO₄. If no NaClO₄ is added, slower formation of [Mn₂O(OAc)₄·(H₂O)(S₂O₇)(bpy)](PF₆)₂ crystals results; the latter contains a bound S₂O₇²⁻ ligand and has been described elsewhere.²²

Description of Structures. The structures of 1, 5, and the anion of 7 are shown in Figure 1, and important interatomic distances and angles are compared in Table II. For complex 1, the two Mn atoms are bridged by two AcO⁻ and one O₂⁻ groups across an intermolecular separation of 3.153(3) Å. A C1- and bpy group complete distorted octahedral geometry at each metal center. The molecule has nonimposed C₂ symmetry, and the C1(3)-Mn(1)-Mn(2)-C1(4) torsional angle is 81.6°. There is clear evidence for a Jahn-Teller elongation (high-spin d⁶ Mn³⁺). The Mn-carboxylate distances fall into two statistically-inequivalent groups differing by over 0.2 Å, and the Mn-C1 distances are remarkably long (2.515, 2.611 Å) for terminal ligands at this oxidation level. In [Mn₂OCl₃(OCR)(py)(py)]⁺ terminal Mn²⁺Cl⁻ distances are a more reasonable 2.24 Å (average).²³ Thus, the Jahn-Teller distortion takes the form of an elongation along the C1(3)-Mn(1)-O(5) and C4(4)-Mn(2)-O(11) axes. In Mn²⁺(TPP)(py)Cl⁺, a similar Jahn-Teller elongation leads to a Mn-Cl distance of 2.467(1) Å.²⁴ The even longer distances in 1 are probably due to the hydrogen bonding with the solvate water molecules (vide infra) but, since both C1(3) and C4(4) are involved in these additional interactions, it is surprising that there is a 0.1 Å difference between Mn(1)-Cl(3) and Mn(2)-Cl(4) distances.

For complex 5, unlike complex 1, the molecule lies on a crystallographically imposed 2-fold axis passing through O3(23), but otherwise the two structures are extremely similar, except that the terminal Cl⁻ atoms have been replaced by two N₃ groups. The Mn⁻⁻Mn separation is 3.153(4) Å, identical to that in 1. The N(24)-Mn(1)-Mn(1)-N(24) torsional angle is 108.2°. Jahn-Teller elongation, along the N(24)-Mn(1)-O(14) axis, is again evident, and indeed, the Mn-C1(3) distance (1.229(9) Å) is long and comparable to the axially-elongated Mn-N₃ distance (2.170(6) Å) in Mn[TACN(N)](PF₆)²⁺ the equatorial Mn-N₃ distances in the latter complex are noticeably shorter (1.911(6) and 1.951(6) Å). There is also a slight, but almost statistically insignificant, difference between the two Mn-N(bpy) distances, suggesting, at most, only a small trans influence by the short Mn-O(23) linkage; in complex 1, the difference is so small as to be insignificant.

For the cation of complex 7, the structure is very similar to those of 1 and 5. The Mn-Mn separation is 3.152(2) Å, and the O(8)-Mn(1)-Mn(2)-O(11) torsional angles is 94.4°. Again, the monodentate terminal ligands, in this case H₂O, lie on Jahn-Teller elongation axes, and there is an insignificant trans influence of the bridging oxide O(5) on the Mn-N(bpy) lengths.

Overall, it is clear that the three structures are very similar, as emphasized in Table II, and that the identity of the terminal monodentate ligand (Cl⁻, N₃⁻, and H₂O) has an almost insignificant structural effect. However, as will be described below, there is a more noticeable and rather interesting influence of these ligands on the magnetic properties of the complexes (vide infra).

The presence of solvent molecules leads to extensive hydrogen-bonding interactions in the lattices of 1, 5-MeCN·4H₂O, and 7. For complex 1, each water molecule links two Mn₃⁺ molecules by hydrogen bonding to Cl(3) of one molecule and Cl(4) of an adjacent molecule. The O(42)--Cl(3) and O(42)--Cl(4) distances are 3.128 and 3.101 Å, respectively. These interactions are then repeated, leading to one-dimensional polymeric chains. The acetic acid molecule is also hydrogen bonding to the water via its OH function (O(42)--O(38) = 2.648 Å) and is not linked to the Mn₃⁺ molecule. For complex 5-MeCN·4H₂O, one of the H₂O molecules links the Mn₂ complexes in a similar fashion as for 1, forming connecting hydrogen bonds to N(24) and N(24)' of two adjacent molecules leading to one-dimensional polymers in the lattice; the O(27)--N(24) distance is 2.87 Å. The remaining H₂O and MeCN solvate molecules are not linked to the Mn₃ groups but are themselves hydrogen bonded via HO···H-NMeCN interactions (O(28)--N(31) = 2.656 Å).

There are now eight structurally-characterized examples of complexes containing the [Mn₂O(OAc)₃Cl]³⁺ bridging unit size 1, 5, 7 (and the PF₆⁻ salt),¹² [Mn₂O(OAc)₃(H₂O)(bpy)](PF₆)₃⁺ [9, Hbpy] = hydrotrios(is(1-pyrazolyl)borate),¹³ [Mn₂O(OAc)₃(TACN)]²⁺ (10, TACN = 1,4,7-triazacyclononane), [Mn₂O(OAc)₂(Me₃TACN)]²⁺ (11, Me₃TACN = 1,4,7-trimethyl-1,4,7-triazacyclononane), [,³][Mn₂O(OAc)₂(TMP)](ClO₄)₂ (12, TMP = triis(N-methylimidazol-2-yl)phosphine),²⁷ and [Mn₂O(OAc)₂(H₂O)(S₂O₇)(bpy)](13). Complex 9 has been characterized as both the mono- and tetrakis-MeCN solvate. Pertinent structural parameters for the bridging unit of these complexes are collected in Table III. It is evident that there are no major differences between these complexes. The replacement of tridentate HBpz⁻, TACN, or TMP with a bidentate bpy and monodentate Cl⁻, N₃⁻, or H₂O thus has no serious effect on the bridging unit. A comparison of the structural parameters of 9 and 10 and their Fe³⁺ analogues has been provided elsewhere.7

Electrochemistry. The electrochemical properties of complexes 1, 2, 3, and 5 have been examined by cyclic voltammetry (CV) in DMF: the choice of the solvent was unfortunately dictated by low solubility of these complexes in other solvents. Complex 1 displays a quasi-reversible oxidation at E₁/₂ = 0.38 V for ferrocene with ΔE₁/₂ = 210 mV at 50 mV/s; the reversible ferrocene couple has ΔE₁/₂ = 100–120 mV under the same conditions. We suspect DMF/Cl⁻ exchange equilibria to be occurring in this solvent, which may account for the broadened features. Complexes 2 and 3 show a similar process at E₁/₂ = 0.41 and 0.40 V, respectively. These features are assigned to the Mn³⁺/Mn²⁺/Mn⁴⁺ couple. This is analogous to behavior already described for other [Mn₃O(O₂CR)₃]³⁺ species which, however, give better-looking cyclic voltammograms; further, the one-electron oxidized form of complex 11 has been isolated and structurally characterized.

Confirming its Mn^{III}Mn^{V} formulation. Complex 5 displays an analogous quasi-reversible oxidation at 0.18 V and an irreversible feature at 0.51 V; the latter is similar to that of NEt_{2}N_{2}S (0.43 V) under comparable conditions and is thus assigned to N_{3} oxidation. Complexes 1, 2, 3, and 5 also show additional oxidation features at higher potentials, but these are not well resolved and/or irreversible. Overall, the effect of N_{3} vs Cl^- is to shift the oxidation potential to less positive values by about 0.2 V. On the reduction side, all complexes show only broad irreversible features in the -0.30 to -1.0 V range.

Magnetic Susceptibility Studies. The variable-temperature solid-state magnetic susceptibilities of [Mn_{2}O(OAc)_{2}Cl_{2}(bpy)]_{2} (1) and [Mn_{2}O(CPh)_{3}(N_{3})_{2}(bpy)]_{2} (5) were measured in the temperature range 5.0 to 330 K. Similar studies on the PF_{6} salt of the cation of 7 have already been reported elsewhere. The effective magnetic moment \mu_{\text{eff}} per Mn^{III} for complex 1 decreases gradually with decreasing temperature from 6.33 \mu_B at 327.7 K to 5.85 \mu_B at 100 K and then more steeply to 2.09 \mu_B at 5.0 K (Figure 2). The effective magnetic moment of complex 5, on the other hand, increases steadily from a value of 6.96 \mu_B at 320 K to a maximum of 8.12 \mu_B at 30 K and then decreases to 7.45 \mu_B at 5.0 K (Figure 3). The magnetic behavior of 1 is that expected for a pair of antiferromagnetically-coupled high-spin (S = 2) Mn^{III} ions, while that observed for 5 is characteristic of a net ferromagnetic interaction between the two Mn^{III} ions. The behavior of \mu_{\text{eff}} at low temperature for 5 is similar to that observed in ferromagnetically-coupled dinuclear Ni^{II} complexes. The increasing moment is due to population of the S = 4 ground state, while the decrease in moment at lower temperatures is due to changes in the populations of the components of the S = 4 ground-state multiplet that are split by contributions from zero-field splitting and Zeeman interactions.

A model was constructed to analyze the magnetic data of 1 and 5 that included in the Hamiltonian for the dinuclear complex the isotropic Heisenberg exchange interaction -2J\mathbf{S}_{1}\cdot\mathbf{S}_{2}, an isotropic Zeeman interaction and the axial zero-field splitting terms, D(S_{z}^{2}) - S(S + 1)/3 (l = 1, 2), for both ions. The Hamiltonian matrix was constructed with a set of uncoupled product basis functions using the program PAIR. The eigenvalues and eigenvectors of the system are evaluated by diagonalization of the 25 x 25 Hamiltonian matrix including the Zeeman terms. The paramagnetic susceptibility \chi of a dinuclear Mn^{III} complex was then obtained from the calculated magnetization using eq 5, where the derivatives of the energy of each level with respect to the magnetic field \delta E/\delta H were calculated from the appropriate eigenvector using the Hellman--Feynman theorem. The whole calculational procedure was incorporated into a nonlinear least-squares fitting computer program and used to fit the temperature dependence of the magnetic moments of 1 and 5 as a function of J (the exchange coupling parameter), D (the single-ion zero-field splitting), and an isotropic g value.

For complex 1, it was found that a good fit of the \mu_{\text{eff}} vs temperature data could be obtained, except at the lowest temperatures where the theoretical values of \mu_{\text{eff}} were found to be smaller than those observed. In the case of antiferromagnetically-coupled complexes, it is frequently the presence of a small amount of paramagnetic impurity that causes this deviation. Thus, in the fitting of the data for complex 1, we included a susceptibility term (Curie law behavior) for a paramagnetic S = 2 impurity. The solid line in Figure 2 illustrates how good this fit is; the fitting parameters are g = 1.88, J = -4.1 cm^{-1} and D = 0.07 cm^{-1} with 0.8% by weight of a paramagnetic S = 2 impurity. It should be emphasized that the value of J is not appreciably influenced by the amount of paramagnetic impurity. On the other hand, it is our experience that the fitting of \mu_{\text{eff}} vs temperature data is not very sensitive to the single-ion zero-field splitting parameter D.

Least-squares fitting of the \mu_{\text{eff}} vs temperature data for complex 5 with the matrix diagonalization approach outlined above gave g = 1.86, J = +8.8 cm^{-1}, and D = 0.3 cm^{-1}. The solid line in Figure 3 represents this fit. It can be seen that there is some deviation between the line that represents the best fit and the experimental data, particularly in the low-temperature region. Data were collected for several samples of complex 5 and were

Figure 1. ORTEP representations of complexes 1 (top), 5 (middle), and the anion of 7 (bottom) at the 50% probability level; bpy C atoms are numbered sequentially from one N atom to the other.
torquing of small crystallites in a magnetic field. So the deviation at low temperatures cannot be attributed to the likely origin of the deviation between the solid line and the experimental data in Figure 3. A figure showing the hydrogen-bonding network is available in supplementary material.

Field-Dependent Magnetization of $[\text{Mn}_2\text{O(OAc)}_2\text{Cl}_2\text{(bpy)}_2] \cdot \text{AcOH} \cdot \text{H}_2\text{O}$ (1) at 10.0 kG. The solid line represents a least-squares fit of the data.

of 10.0 and 50.0 kG in the range of 2.0–30.0 K to characterize further the ground state of this complex. Figure 4 shows a plot of effective magnetic moment versus temperature for the data collected at either 10.0 or 50.0 kG field. It can be seen that increasing the magnetic field from 10.0 to 50.0 kG leads to a greater effect for the Zeeman interaction. The value of $\mu_{\text{eff}}$ is reduced owing to saturation effects.

The 10.0 and 50.0 kG low-temperature $\mu_{\text{eff}}$ data observed for complex 5 were simultaneously least-squares fit to the matrix diagonalization model described above for fitting the full temperature dependence of the susceptibility data measured at 10 kG. The two solid lines in Figure 4 result from such a least-squares fit, which gives the parameters $g = 1.86, J = +8.8$ cm$^{-1}$, and $D_1 = D_2 = 0.3$ cm$^{-1}$. The fit is reasonable in view of the above-mentioned possible intermolecular interactions. Clearly, complex 5 has an $S = 4$ ground state.

A value of $D = 0.3$ cm$^{-1}$ for the axial zero-field splitting in the $S = 4$ ground state of complex 5 is probably in the range expected for a $\text{Mn}^{III}$ complex. Of course, the magnitude of $D$ for the $S = 4$ state reflects the magnitude of the axial single-ion zero-field interaction parameters at each $\text{Mn}^{III}$ ion. A $\text{Mn}^{III}$ ion in a tetragonally-elongated coordination site with $C_4$ symmetry will have a $^3\Sigma_1$ (e$^2$e$b^1_3$) ground state with $^3\Delta_1$ (e$^2$b$^2_1$), $^3\Sigma_2$ (e$^2_a^1$b$^1_2$), and $^3\Sigma_0$ (e$^2_a^1$b$^1_3$) excited states. The $^3\Sigma_0$ and $^3\Sigma_2$ excited states can interact with the $^3\Sigma_1$ ground state to give a zero-field splitting of the $^3\Sigma_1$ state into levels with $M_S = 0, \pm 1,$ and $\pm 2$. When $D < 0$, the $M_S = \pm 2$ level is at the lowest energy, whereas when $D > 0$, then the $M_S = 0$ level is at the lowest energy. Depending on the magnitudes of distortion and crystal field interactions, triplet states can also be involved in a spin-orbit interaction with the $^3\Sigma_1$ ground state. $D$ values for Schiff-base and porphyrin complexes of $\text{Mn}^{III}$ have been found to fall in the range of −1.0 to −3.0 cm$^{-1}$.

Magnetostuctural Commentary. The magnitude of the magnetic exchange interactions between the two $\text{Mn}^{III}$ ions found in complexes 1 and 5 may be compared with those reported for the other $\text{Mn}^{III}$ complexes that have the $[\text{Mn}_2\text{O}(\text{O}_2\text{CPh})_2]^{2+}$ bridging unit. As summarized in Table III, the $\text{Mn}^{III}$ ions are antifer-
sought to identify the subtle structural differences between 5/11 and the other complexes that result in the former pair being ferromagnetically coupled. However, no clear-cut trends are obvious. The Mn–O–Mn angles and Mn–O lengths in 5 and 11 are very slightly smaller and greater, respectively, than for complexes with negative J values. However, applying strictly the statistical 3σ criterion for esds makes all these values insignificantly different.

Since peripheral ligands are also varying, further discussion is restricted to the subset of complexes 1, 5, and 7, varying only in one ligand per Mn. These complexes have J values spanning a range of ~13 cm⁻¹, and one might normally be tempted to conclude that, within experimental variation, the complexes are essentially indistinguishable magnetically. But, of course, a distinct difference does indeed exist between them in that 5 is ferromagnetically coupled, whereas 1 and 7 are antiferromagnetically coupled; this difference is real and cannot be ignored as due to experimental variation. Thus, we feel duty-bound to attempt a rationalization of the differences between 5 and 1/7 based on the structures of the three complexes. As described above and in Table III, the three structures are essentially superimposable except for the terminal monodentate ligands (N₃⁻, Cl⁻, or H₂O). As is customary in discussing oxide-bridged dimers, each z axis is placed along the Mn–O bond (see below). The

<table>
<thead>
<tr>
<th>complex</th>
<th>Mn–Mn, Å</th>
<th>Mn–O, Å</th>
<th>Mn–O–Mn, deg</th>
<th>J, cm⁻¹</th>
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<td>1</td>
<td>1.788(11)</td>
<td>1.777(12)</td>
<td>1.535(3)</td>
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<td>1.512(3)</td>
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<tr>
<td>9</td>
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<td>1.512(3)</td>
<td>1.154(1)</td>
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<td>1.512(3)</td>
<td>1.154(1)</td>
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</tbody>
</table>

* Observations using the -S_i-2;S_i-2 convention. 
* This work. 
* PF₅⁻ salt, all data from ref. 12. 
* MeCN salt, all data from ref. 12. 
* Quoted range -0.2 to -0.7 cm⁻¹ for both solvent forms. 
* Similar to 9; na = not available.

romagnetically coupled in 1, the PF₅⁻ version of 7, [Mn₂O₂(OAc)₂(H₂O)_4] [9] and [Mn₂O₂(OAc)₂(TMIP)₂]ClO₄ [12] and ferromagnetically coupled in 5 and 7, and none of the terminal monodentate ligands (N₃⁻, Cl⁻, or H₂O). As is customary in discussing oxide-bridged dimers, each z axis is placed along the Mn–O bond (see below).

In Table III, we compare the structural parameters of the oxide-bridged core, viz. the Mn–Mn distance, and the Mn–O distances and Mn–O–Mn angles. It is clear that the Mn–Mn separation is not a factor in determining the precise value of J, complexes 1 and 5 having identical values but different signs of J. It should be emphasized that for all [Mn₂O₂(OAc)₂]¹⁺ species, the exchange interactions are extremely weak. Further, the J values only span a range of ~13 cm⁻¹. Since the exchange interaction in a d₄–d₄ dimer will be the net sum of various antiferromagnetic and ferromagnetic contributions, it is not anticipated that a correlation of J with a single structural parameter will exist. The overall weak couplings have been rationalized at a qualitative level by consideration of the symmetry of the pair of overlaps of the magnetic orbitals; this has also provided a useful guide to the variation of J with M⁺⁺ (and d⁴⁺) across the first transition series. In the present case, we have

Discussion and Biological Relevance

Synthetic procedures have been devised that allow convenient access routes to dinuclear complexes containing the $\text{[Mn}_2\text{O(O}_2\text{CR})_2]\text{H}_2\text{O}$ bridging unit and terminal bpy groups. A sixth coordination site is thus available at each Mn for binding additional monodentate groups, and the preparation of the $\text{Cl}^-$, $\text{N}_3^-$, and $\text{H}_2\text{O}$ complexes is readily accomplished. Employment of tridentate capping ligands is thus clearly not a prerequisite for stabilizing the $\text{[Mn}_2\text{O(O}_2\text{CR})_2]\text{H}_2\text{O}$ core, although complexes with tridentate ligands do seem more robust with respect to redox changes, as evidenced by their more ideal and reversible electrochemical behavior when studied by cyclic voltammetry. Structurally, the several crystallographically-characterized complexes are essentially superimposable, except for the identity of their peripheral ligands.

If, as is currently thought, the dinuclear site of Mn catalase (and, possibly, also Mn ribonucleotide reductase) involves a similar $\text{[Mn}_2\text{O(O}_2\text{CR})_2]\text{H}_2\text{O}$ core, it is likely that substrate binding sites in peripheral positions will also be present. This would be as already established for the related Fe$_{2}$biomolecules, hemerythrin (Hr), and Fe ribonucleotide reductase. In addition, again, as for hemerythrin, further study of Mn catalase may possibly lead to the preparation of various substrate–analog-bound forms viz. $\text{Cl}^-$, $\text{N}_3^-$, aquo-catalase (which may be the resting form of the enzyme), and possibly others, containing the indicated exogenous terminal ligands. Indeed, we note that both $\text{Cl}^-$ and $\text{N}_3^-$ are reported to be inhibitors of Mn catalase. Although $\text{N}_3^-$ only weakly inhibits the $T$–album enzyme, it is a more potent inhibitor of the $T$. thermophilus catalase. More recently, the $L$. plantarum enzyme is also reported to be inhibited by azide.

The conclusion from these studies is that $\text{N}_3^-$ bonds to the Mn. Similar conclusions were reached from parallel studies employing SCN$^-$ and $\text{F}^-$, and it therefore appears that a variety of exogenous ligands are capable for ligating to the Mn. Thus, the series 1, 5, and 7 may prove of some utility in the future as models for some of these various enzyme forms.

With the above in mind, we have felt it particularly important to characterize 1 and 5 by magnetic susceptibility studies to complement data already available for the PF$_6^-$ version of 7. As might have been expected, the $\text{Cl}^−$/$\text{N}_3^−$/$\text{H}_2\text{O}$ variation has very little effect on the overall exchange interaction between the Mn$^{III}$ sites, giving values spanning a range of only 13 cm$^{-1}$. However, the exchange interactions are very weak (ca. zero), this range is sufficient to have an apparently large effect in leading to a ferromagnetic interaction in complex 5 and a $S = 4$ ground state, in contrast to antiferromagnetically-coupled 1 and 7 and their $S = 0$ ground states. It is proposed that the sensitivity of the exchange interaction to the monodentate terminal ligands is due to exchange pathways involving the $d_{\pi}$ orbitals with the oxide and the $d_{\sigma}$ orbitals with the bridging carboxylate groups. Since substrate–analog forms of the catalase, should they become accessible, will have identical ligation sets except for the exogenous ligands, it will be interesting to see whether similar variations in the sign of $J$ will be encountered.

It should be mentioned that the most extensive set of complexes containing the $\text{[Mn}_2(\mu-O)(\mu-O_2\text{CR})_2]$ core for which magneto-